Journal of Organometallic Chemistry 696 (2011) 3015-3022

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis and structure of new Schiff base derivatives obtained from 2-(formylphenyl)mercury bromide

Rajesh S. Baligar^a, Sagar Sharma^a, Harkesh B. Singh^{a,*}, Ray J. Butcher^b

^a Department of Chemistry, Indian Institute of Technology Bombay, Powai 400076, Mumbai, India ^b Department of Chemistry, Howard University, Washington, DC 20059, USA

ARTICLE INFO

Article history: Received 14 January 2011 Received in revised form 20 April 2011 Accepted 2 June 2011

Keywords: Organomercury Mercuration Metallamacrocycle Intramolecular interaction Anion binding

ABSTRACT

Reactions of (2-formylphenyl)mercury(II) bromide **10** with primary amines give *mono-*, *bis-* and *tris-*Schiff base derivatives (**11–18**). Structures of the synthesized compounds show the presence of fivemembered intramolecular Hg…N interaction. Luminescence studies of the compounds have been performed. Attempts to use the synthesized compounds for binding neutral donor molecules or fluoride ions were unsuccessful.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Arylmercury chlorides with in-built donor atoms, capable of forming 5-membered rings, have been extensively studied due to; (i) their applications in the synthesis of other organometallic compounds via transmetallation [1–9], (ii) observation of chirality due to mercury as a stereocentre [10,11], and (iii) luminescence properties [12]. o-Mercurated compounds with in-built N-donor functionalized aromatic ligands are known to exhibit Hg...N secondary interactions. The typical examples of o-mercurated halides with 5-membered Hg…N interactions include (Fig. 1); (2-(pyridin-2-yl)phenyl)mercury(II) chloride (1) [13], (2-(phenyldiazenyl)phenyl)mercury(II) chloride (2) [14], [2-(dimethylaminomethyl) phenyl]mercury(II) chloride (3) [15], (2-((dimethylamino) ethyl)phenyl)mercury(II) chloride (4) [15], o-mercurated ferrocenyl amines (6) [16-18], and imines (7) [19] etc. Although scores of organomercury halides having Hg…N intramolecular interaction are known in the literature, a search in Cambridge Crystallographic Database reveals that the structurally characterized bromide analogs are rare.

The intramolecular $Hg \cdots N/O$ interactions are generally weak. In some of these intramolecularly coordinated compounds, the

* Corresponding author. Fax: +91 022 25767152.

E-mail address: chhbsia@chem.iitb.ac.in (H.B. Singh).

mercury atom is out of plane i.e. slightly pyramidal and becomes chiral [10]. Our group has been interested in the study of weak Hg…N/O/Hg interactions and has investigated these by structural and theoretical studies [20–22]. We thought it worthwhile to systematically investigate the nature of Hg…N intramolecular interactions in a series of mono-, bis- and tris- Schiff base derivatives derived from 2-(formylphenyl)mercury bromide and also probe the presence/absence of mercury as a stereocentre. The bisand tris-Lewis acidic arylmercury bromides can also serve as suitable hosts for binding anions. In this paper we report the first isolation of an intramolecularly coordinated arylmercury bromide in enantiomerically pure form, which is chiral without a chiral center. We also report on the nature of Hg…N interaction in the synthesized compounds.

2. Results and discussion

2.1. Synthesis

Precursors **8** and **9** were prepared from 2-bromobenzaldehyde by following the literature procedure. (Scheme 1) [23,24]. The reaction of the intermediate, (2-(1,3-dioxolan-2-yl)phenyl)magnesium bromide obtained from **8** with 1 equivalent of HgBr₂ yielded **9**, which on subsequent reaction with *p*-toluenesulfonic acid monohydrate, gave **10**. The synthesis of the mono-Lewis acidic Schiff bases **11–14** was accomplished by the condensation reactions of **10**





⁰⁰²²⁻³²⁸X/\$ – see front matter @ 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.jorganchem.2011.06.001



Fig. 1. Representative examples of o-mercurated halides



Scheme 1. Synthesis of compounds 11-14.

with various monoamines (Scheme 1). Similarly, refluxing **10** with diamines and triamine led to the formation of a series of bis- and tris-Lewis acidic Schiff bases (**15–18**) (Scheme 2). Except the bis-Lewis acid derivative **17**, which is yellow in colour, the other derivatives were obtained as off-white solids. The Schiff bases obtained are sparingly soluble in chloroform, acetone, DMSO and



Scheme 2. Synthesis of compounds 15-18.

insoluble in alcohol. All the compounds are air- and moisture stable for weeks both in the solid state as well as in solution.

2.2. Molecular structures of 10, 11, 12, 13, 17 and 18

The molecular structure of **10** is depicted in Fig. 2a. Compound **10** crystallizes in P_{21}/c space group. The coordination geometry around mercury is T-shaped with C1–Hg–Br bond angle being 177.8(3)° (Table 1). The intramolecular Hg…O distance is 2.820(9) Å. This is close to the value 2.824(7) Å reported for the corresponding chloro- analog of **10** [25]. It is interesting to note that the Hg atom in **10** exhibits both intermolecular as well as intramolecular interactions with oxygen atom of the aldehydic group. The intermolecular Hg…O distance (2.943(9) Å) is shorter than the sum of the van der Waals radii of mercury (1.73–2.05 Å) [13,26,27] and oxygen (1.52 Å) [28]. This intermolecular interaction leads to expansion along the *c* axis to give a one dimensional wavy network of Hg–O bonds (Fig. 2b).

Compound **11** crystallizes in orthorhombic crystal system with $P2_12_12_1$ chiral space group (Fig. 3). The coordination geometry around Hg is T-shaped with C1–Hg–Br bond angle of 176.6(4)° (Table 1). The slight deviation of C1–Hg–Br bond angle from linearity can be attributed to the stronger secondary interaction of the imine nitrogen with mercury. The Hg…N distance of 2.685(12) Å is significantly less than sum of the van der Waals radii of mercury (1.73–2.05 Å) [13,26,27] and nitrogen (1.55 Å) [28], however, considerably longer than the sum of their covalent radii (2.03 Å) [29]. It is also worth noting that the Hg…N distance of 2.685(12) Å is shorter than that observed in [2-(dimethylaminomethyl)phenyl] mercury(II) chloride (2.764(6) Å) [15], and 2-chloromercuro-1-[(4-methoxyphenylimino)methyl] ferrocene (2.897(2) Å) [19].

In similar compounds, chirality has been observed due to mercury being a stereocentre where mercury is out of the plane of surrounding attached atoms [10]. However, for compound **11**, it is not the case and the mercury atom is coplanar with the atoms bonded to it. However, the phenyl ring bonded to N is not planar with the rest of the molecule and this conformation results in axial chirality. The phenyl ring bonded to N has a twist angle of 13.1° from the rest of the molecule. This twist is due to the a strong intramolecular coordination of the imine N to Hg. Due to this, the N atom is not in the plane with the N-phenyl ring of the molecule. The molecule has "P" chirality.

The molecular structure of compound **12** is shown in Fig. 4. It is interesting to note that compound **12** exists as dimer in the solid state that gives rise to a 10-membered macrocyclic structure. The mercury atoms in the macrocyclic structure are 4-coordinated and have a distorted tetrahedral geometry. The expected linearity of C–Hg–Br bond angle is lost and it has a value of $163.66(16)^\circ$. This deviation from linearity is highest in the series. This significant deviation from the linearity is due to coordination of the terminal nitrogen of one unit of the dimer with the mercury atom (N2…Hg# and N2#…Hg) of the other half of the dimer. Also it is noteworthy that the intermolecular Hg…N2# distance of (2.658(5) Å) is shorter than the intramolecular Hg…N1 distance of 2.776(6) Å in **12** (Table 2).



Fig. 2. (a) Molecular structure of 10 at 50% thermal ellipsoidal probability. (b) Intermolecular and Intramolecular Hg. O interaction in 10.

Compound **13** crystallizes in triclinic crystal system with *P*-1 space group. It has two molecules in the asymmetric unit. In one of the two molecules, the propyl side chain is disordered over two conformations. The geometry around mercury is T-shaped in both the units and the N…Hg distances are 2.678(7) and 2.706(7) Å (Fig. 5a). Similarly C–Hg–Br bond angles have values of 179.4(2) and 174.4(3)°. It is clearly evident that the higher deviation of C–Hg–Br bond angle in one of the molecules of the asymmetric unit is due to the stronger coordination of the imine nitrogen to mercury. This forces the mercury to attain a bent geometry rather than the ideal linear arrangement. Apart from Hg…N interaction, Hg is involved in two types of Hg…Br interactions; a very weak Hg…Br interactions within the coplanar molecules of asymmetric unit (3.647(7) Å) and a stronger interaction with the adjoining coplanar group at 3.428(14) Å. The Hg…Br distance of 3.428(14) Å is

 Table 1

 Comparision of selected experimental bond lengths (Å) and angles (°) of compounds

 10
 11 and 17 with calculated values

| | Crystal parameters | Optimized parameters |
|----------|--------------------|----------------------|
| 10 | | |
| Hg-Br | 2.4366(13) | 2.4619 |
| Hg-C1 | 2.072(11) | 2.1002 |
| Hg-01 | 2.820(9) | 2.7841 |
| C1-Hg-Br | 177.8(3) | 176.04 |
| O1-Hg-Br | 108.0(2) | 111.76 |
| C1-Hg-01 | 72.0(4) | 72.19 |
| C7-01-Hg | 98.1(8) | 101.71 |
| 11 | | |
| Hg—N | 2.4439(19) | 2.4960 |
| Hg–C1 | 2.037(16) | 2.1204 |
| Hg—Br | 2.685(12) | 2.7293 |
| C7-N | 1.29(2) | 1.2827 |
| C1–Hg–Br | 176.6(4) | 176.09 |
| N–Hg–Br | 109.5(3) | 110.23 |
| C1-Hg-N | 73.9(5) | 73.41 |
| C7–N–Hg | 102.2(9) | 102.67 |
| C8–N–Hg | 134.0(10) | 135.34 |
| C7-N-C8 | 123.4(13) | 121.98 |
| C6–C1–Hg | 120.3(11) | 117.8 |
| 17 | | |
| Hg–Br | 2.455(3) | 2.4783 |
| Hg–C1 | 2.140(10) | 2.1000 |
| Hg—N | 2.767(9) | 2.7484 |
| C7–N | 1.243(13) | 1.2813 |
| Hg—Hg# | 4.019(8) | 4.9165 |
| C8-N | 1.426(14) | 1.4072 |
| C1–Hg–Br | 175.8(3) | 175.74 |
| N–Hg–Br | 112.54(17) | 111.16 |
| C1-Hg-N | 71.6(3) | 73.06 |
| C7–N–Hg | 100.3(8) | 102.39 |
| C8–N–Hg | 138.6(6) | 135.79 |
| C7-N-C8 | 120.8(10) | 120.98 |
| C6–C1–Hg | 118.5(7) | 118.77 |
| | | |



Fig. 3. Molecular structure of 11 at 50% thermal ellipsoidal probability.

less than the sum of the van der Waals radii of mercury and bromine $(\sum vdW (Hg, Br) = 3.59-3.90 \text{ Å})$, however, the Hg...Br distance of 3.647(7) Å is higher than the lower range of sum of van der Waals radii of mercury and bromine. It leads to the formation of a loosely associated tetramer. (See Supplementary Information Fig. S1). Compound **13** is also involved in intermolecular hydrogen bonding in the solid state through the interaction of alcoholic oxygen of OH group of one molecule with hydrogen atom of OH group of other molecule with the distances being 2.15 Å and 1.79 Å (Fig. 5b).

The molecular structure of **17** is depicted in Fig. 6. Compound **17** crystallizes in monoclinic crystal system with C2/c space group. Both the mercury atoms have nearly T-shaped geometry with C1–Hg–Br and N–Hg–Br bond angles being 175.8(3)° and 112.54(7)° respectively. The intramolecular N…Hg distance of 2.767(9) Å is highest among all the synthesized compounds. The two mercury atoms are at a distance of 4.019(8) Å from each other which is higher than sum of the covalent radii of mercury (2.64 Å) [29] but is closer to upper range of sum of van der Waals radii of



Fig. 4. Molecular structure of 12 in metallamacrocycle form at 30% thermal ellipsoidal probability.

| Table 2 | |
|---|---|
| Selected bond distances (Å) and angles (°) for $12,13$ and 13 | 8 |

| 12 | | | |
|-------------|------------|-------------|------------|
| Hg—Br | 2.4863(7) | Hg-C1 | 2.072(5) |
| Hg-N1 | 2.776(5) | Hg-N2# | 2.660(5) |
| C1–Hg–Br | 163.68(16) | N1–Hg–Br | 104.23(10) |
| C1-Hg-N1 | 73.6(2) | C1-Hg-N2# | 106.31(19) |
| N2#-Hg-Br | 90.00(10) | C7–N1–Hg | 100.3(4) |
| C8–N1–Hg | 141.0(4) | C7-N1-C8 | 118.0(5) |
| C6-C1-Hg | 118.7(4) | | |
| 13 | | | |
| Hg1–Br1 | 2.4452(11) | Hg2–Br2 | 2.4422(12) |
| Hg1–C1A | 2.092(7) | Hg2–C1B | 2.101(8) |
| Hg1–N1A | 2.706(7) | Hg2–N1B | 2.678(7) |
| C1A-Hg1-Br1 | 179.4(2) | C1B-Hg2-Br2 | 174.3(2) |
| N1A-Hg1-Br1 | 107.10(18) | N1B-Hg2-Br2 | 107.29(16) |
| C7A–N1A–Hg1 | 101.1(6) | C7B-N1B-Hg2 | 102.1(7) |
| C1A–Hg1–N1A | 73.4(3) | C1B-Hg2-N1B | 74.0(3) |
| C2A-C1A-Hg1 | 121.1(8) | C2B-C1B-Hg2 | 121.1(5) |
| C7A-N1A-C8A | 120.7(11) | C7B-N1B-C8B | 122.2(7) |
| 18 | | | |
| Hg1–Br1 | 2.4410(17) | Hg2–Br2 | 2.4350(17) |
| Hg3–Br3 | 2.422(2) | Hg1–C1A | 2.089(14) |
| Hg2–C1B | 2.079(15) | Hg3–C1C | 2.063(16) |
| Hg1–N1A | 2.717(13) | Hg2–N1B | 2.661(11) |
| Hg3–N1C | 2.670(11) | | |
| C1A-Hg1-Br1 | 176.3(4) | C1B-Hg2-Br2 | 173.8(3) |
| C1C-Hg1-Br3 | 176.1(4) | N1A-Hg1-Br1 | 107.4(3) |
| N1B-Hg2-Br2 | 104.7(3) | C7C-N1C-Hg3 | 103.3(9) |
| C7B–N1B–Hg2 | 99.6(9) | C1B-Hg2-N1B | 75.7(5) |
| C1A-Hg1-N1A | 74.3(5) | C6A-C1A-Hg1 | 118.0(12) |
| C1C-Hg3-N1C | 73.9(5) | C6C-C1C-Hg3 | 118.3(10) |
| C6B-C1B-Hg2 | 116.2(12) | | |

mercury (\sum_{vdW} (Hg, Hg) = 4.1 Å). One of the most remarkable features of the molecule is the conformation adopted about the imine bonds. In contrast to the expected coplanarity of imine groups with the phenyl ring, here again the imine group is rotated by 43° out of this plane. This is probably due to the intramolecular coordination of the imine N to the Hg.

The molecular structure of compound **18** is tripodal shaped (Fig. 7). It crystallizes as a dichloromethane solvate in monoclinic crystal system with P2₁/c space group. The Hg atoms are at a distance of 7.306(4)–7.561(2) Å from each other which excludes any weak Hg…Hg interaction between them. The Hg…N distances in **18** range from 2.661(11) Å to 2.717(13) Å. The Hg…N distances in the molecular structure of the synthesized compounds are less than the Hg…N distances of related bis(aryl)mercury(II) (2.798(7) Å) [30], bis(2-(((dimethylamino)methyl)phenyl)mercury(II) (2.89(1) Å) [31], bis(2-(((4-methylphenyl)imino)methyl) phenyl)mercury(II) (2.854(2) Å) [23]. The shortening of Hg…N bond distances in the synthesized organomercury bromides,

demonstrates clearly that the electron withdrawing Br ligand strengthens the Hg–N bonding.

2.3. Absorption and emission spectroscopy

The UV-visible spectra for all the compounds (10–18) were recorded in the solid state as well as in the solution state $(3.5 \times 10^{-5} \text{ M})$ at room temperature. In the solution state, the absorption spectrum for the precursor aldehyde, (2-formylphenyl) mercury(II) bromide (10), showed an absorption maxima at 301 nm $(\varepsilon = 2092 \text{ M}^{-1} \text{ cm}^{-1})$. The absorption spectra for the Schiff bases do not show any significant shift in the absorption maxima. A high energy band in the region of 293-307 nm was observed for the Schiff bases. The molar extinction coefficients of 22557 M⁻¹ cm⁻¹ (11) and 22557 M⁻¹ cm⁻¹ (17) are primarily due to π - π * transitions. The solid state UV-visible spectra of the aldehyde 10 showed a broad peak at 351 nm. For Schiff bases having aliphatic chain attached to the imine nitrogen, the absorption maxima appeared in the range of 302-329 nm. For aromatic Schiff base 11, this absorption maximum shifts towards longer wavelength (387 nm), which may be a consequence of the increase in the delocalization of electrons.

The solution state emission spectra of the Schiff bases do not show luminescence which may be due to the quenching of the emission in solution. However, in the solid state, on excitation at λ_{max} of the respective compounds, weak luminescence was observed in the visible region. By exciting at 387 nm in solid state, the emission spectrum of **11** exhibits peaks at 422, 442, 483 nm. All the Schiff bases showed a weak emission band in the region of 400–500 nm.

2.4. Binding studies with electron rich molecules and F^- ions

The presence of Lewis acidic centers in the synthesized compounds prompted us to study the binding of these compounds with electron rich molecules such as DMSO, acetone as well as fluoride anions. The UV–visible titrations of compounds (**11–18**) with fluoride ion did not show any significant binding. Also attempted complexation with acetone or DMSO was not successful. One of the reasons for the lack of binding of these compounds to electron rich molecules may be the partial gain in electron density on mercury by coordination with nitrogen. Also the reluctance of bis- and tris-organomercuro Lewis acids (**15–18**) to binding may be attributed to the large separation the mercury centers which cannot come closer to each other for proper binding with F[–]anions.

2.5. Computational studies

The geometry of the compounds were optimized with SDD basis set for Hg and 6-31g(d) basis set for the remaining atoms. In



Fig. 5. (a) Molecular structure of 13 at 50% ellipsoidal probability showing asymmetric unit containing two molecules (b) Intermolecular hydrogen bonding in 13.



Fig. 6. Molecular structure of 17 at 50% ellipsoidal probability.

general the DFT optimized geometries of all the compounds are in good agreement with the crystal structures. A comparison of the selected values of bond lengths and angles for **10**, **11** and **17** is shown in Table 1. In case of **17** the Hg–Hg# distance in optimized geometry is overestimated by about 0.90 Å. This may be due to the crystal packing effect in the solid state as the calculations have been carried out in gas phase. However, on performing Atoms in Molecules analysis on the crystal geometry of **17**, a bond critical point was located between the two Hg atoms indicating the presence of weak Hg…Hg interaction in **17** (See Supplementary Information Fig S2). The Hg…Hg interaction in **17** is weaker than mercurophilic interactions reported in the literature [32,33].

We also investigated the nature of the secondary Hg…N intramolecular interaction. The NBO interaction energy for the compounds is in the order of 2.5–3 kcal/mol. The secondary Hg…N interaction arises due to the donation of electron density from the lone pair of nitrogen to the σ^* orbital of Hg–C bond. A representative diagram showing such an interaction is shown in Fig S3 (See Supplementary Information).

The UV–Visible absorption spectral behavior by the compounds has been studied by TD-DFT calculations. TD-DFT calculations on



Fig. 7. Molecular structure of 18 at 50% ellipsoidal probability.

3. Conclusion

Compounds **11–18** are the first examples of Schiff bases synthesized from organomercury bromide **10**. All the Schiff bases have imine nitrogen coordinated to the mercury center which perturbs the linearity of the C–Hg–Br angle. The origin of secondary N…Hg interaction is the donation of electron density from lone pair of nitrogen to antibonding σ^* orbital of Hg–C bond. Compound **12** exists as a dimer in solid state and can be called as 10-membered metallamacrocycle. We were successful in isolating an intramolecularly coordinated arylmercury bromide (**11**) in enantiomerically pure form which has axial chirality. The molecule has "P" configuration.

4. Experimental

4.1. General experimental methods

All reactions were carried out under nitrogen or argon atmosphere using standard vacuum-line techniques. Solvents were purified by standard procedures and were freshly distilled prior to use. Melting points were recorded in capillary tubes. ¹H (399.88 MHz), ¹³C (100.56 MHz) NMR spectra were recorded on a Varian 400 MHz spectrometers at room temperature. Chemical shifts cited were referenced to TMS (¹H, ¹³C) as internal standard. FT-IR spectra were recorded on an FT-IR spectrophotometer with KBr pellets. Elemental analyses were performed on a Carlo-Erba model 1106 elemental analyzer. The Electro-spray mass spectra (ES-MS) were performed in a Q-Tof micro (YA-105) mass spectrometer. Mass spectra were obtained with a Platform II single quadrupole mass spectrometer (Micromass, Altrincham, UK) using a CH₃OH mobile phase. All UV-Vis spectra were recorded on a Jasco-570 spectrophotometer. Emission experiments were carried out using a Perkin-Elmer LS55 luminescence spectrometer.

4.2. Syntheses

Caution!: The reactions involving mercury compounds were carried out in a well ventilated fume hood with proper precaution due to their hazardous nature.

4.2.1. Synthesis of compound 9

In a 250 mL three- necked round bottomed flask under N₂ atmosphere, was taken Mg (0.33 g, 13.5 mmol). A few crystals of iodine and 50 mL of THF were added. A solution of 2-(2bromophenyl)-1,3-dioxolane (3.11 g, 13.5 mmol) in 15 mL THF was added drop-wise with the aid of a dropping funnel for a period of 30 min. The resulting reaction mixture was refluxed for 2 h and then cooled to the room temperature. To the ice-cooled reaction mixture at 0 °C, a THF solution of HgBr₂ (4.83 g, 13.5 mmol) was added drop-wise over a period of 1 h. The temperature was allowed to cool to the room temperature. After stirring for 22 h at room temperature, the reaction mixture was treated with 50 mL saturated solution of NH₄Cl. The organic layer was separated and the aqueous layer was extracted with toluene. Both the organic fractions were combined, dried over anhydrous Na₂SO₄, filtered and evaporated under vacuum. The residue was treated with ethanol to yield an off-white solid of 9 (4.08 g, 70% yield). M.p 185-187 °C.

4.2.2. Synthesis of compound 10

In a 250-mL two-necked flask containing100 mL acetone, was added compound 9 (4.08 g, 9.5 mmol), p-toluenesulfonic acid monohydrate (0.20 g, 1.1 mmol) and refluxed for 5 h. The volume of the reaction mixture was reduced to 20 mL on a rotary evaporator and distilled water was added to it. The precipitate so obtained was filtered, washed with distilled water and dried under vacuum to get (2-formylphenyl)mercury(II) bromide as a off-white solid. It was further purified by recrystallization with ethanol (3.45 g, 66% yield). M.p 170-172 °C. Anal. Calcd for C7H5BrHgO: C, 21.80; H, 1.30. Found: C, 21.83; H, 0.95; FT-IR (KBr) 3436, 3061, 1671, 1662, 1575, 1561, 1202, 849, 756 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 10.13 (s, 1H), 7.88 (dd, J = 7.6, 1.2 Hz, 1H.), 7.73 (td, J = 7.4, 1.3 Hz, 1H,), 7.59–7.55 (m, 2H,); ¹³C NMR (400 MHz, CDCl₃): δ 194.1, 151.3, 140.6, 137.7, 136.1, 136.0, 129.8; ES-MS *m*/*z* (relative intensity, nature of peak) 387.1 (100, $[M + 1]^+$; UV–Vis (dichloromethane, λ_{max} nm $(cm^{-1}); \epsilon, M^{-1} cm^{-1})$: 301 (32258); 2092; UV/Vis (solid): λ_{max} : 351 nm; Emission (solid): 420, 456, 483 nm (λ_{ex} 351 nm).

4.2.3. Synthesis of compound 11

In a 50 mL two-necked round bottomed flask, (2-formylphenyl) mercury(II) bromide 10 (0.200 g, 0.52 mmol) was taken and 12 mL of absolute ethanol was added. The reaction mixture was refluxed to give a clear solution. To this clear solution, an ethanolic solution (6 mL) of aniline (0.048 g, 0.52 mmol) was added drop-wise over a period of 8 min. After complete addition of the amine solution, the resulting clear solution was refluxed with stirring, at ~ 100 °C for 48 h. Then the volume of the pale vellowish solution was reduced and kept at room temperature. The off-white crystalline product was collected by filtration, washed with small amount of ethanol, dried under vacuum (0.16 g, 66% yield). M.p 140-142 °C. Anal. Calcd for C₁₃H₁₀BrHgN: C, 33.89; H, 2.19; N, 3.04. Found: C, 34.22; H, 1.70; N, 3.37; FT-IR (KBr) 3047, 2923, 1621, 1583, 1557, 1526, 1185, 765, 714, 686 cm $^{-1};~^{1}\text{H}$ NMR (400 MHz, CDCl_3) δ 8.77 (s, 1H), 7.63–7.28 (m, 9H); ¹³C NMR (400 MHz, CDCl₃) δ 160.8, 150.9, 148.6, 140.4, 137.8, 133.9, 133.1, 129.6, 129.3, 127.4, 121.7; ES-MS m/z (relative intensity, nature of peak) 461.8 (100, $[M + 1]^+$); UV–Vis (dichloromethane, λ_{max} nm (cm⁻¹); ε , M⁻¹ cm⁻¹): 299 (33444); 11473; UV/Vis (solid): λ_{max}: 387 nm; Emission (solid): 442, 483, 765 nm (λ_{ex} 387 nm).

4.2.4. Synthesis of compound 12

A 50 mL two-necked flask was charged with (2-formylphenyl) mercury(II) bromide (0.200 g, 0.52 mmol) in 12 mL of absolute ethanol. To this solution, an ethanolic solution (5 mL) of N, Ndimethylethylenediamine (0.046 g, 0.52 mmol) was added dropwise over a period of 8 min with vigorous stirring. After complete addition of the amine solution, the resulting colorless solution was refluxed at 100 °C for 28 h. The pale yellow solution obtained was reduced under vacuum and kept at room temperature for crystallization. The resulting microcrystalline solid was collected by filtration, washed with ethanol and dried under vacuum (0.14 g, 61% yield). M.p 144–146 °C. Anal. Calcd for C₁₁H₁₅BrHgN₂: C, 28.99; H, 3.32; N, 6.15. Found: C, 29.27; H, 2.50; N, 6.85; FT-IR (KBr) 3051, 2971, 2940, 2857, 1642, 1459, 1212, 1039, 758 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.49 (s, 1H), 7.49–7.37 (m, 4H), 3.82 (t, J = 5.5 Hz, 2H), 2.80 (t, J = 5.4 Hz, 2H), 2.30 (s, 6H); ¹³C NMR (400 MHz, CDCl₃, ppm) 163.9, 163.7, 150.1, 140.1, 137.4, 132.4, 128.8, 59.2, 57.9, 45.6; ES-MS *m*/*z* (relative intensity, nature of peak) 456.9 (100, $[M + 1]^+$); UV–Vis (dichloromethane, λ_{max} nm (cm⁻¹); ε , M^{-1} cm⁻¹): 298 (33557); 1909; UV/Vis (solid): λ_{max} : 329 nm; Emission (solid): 421, 446, 457, 483 nm (λ_{ex} 329 nm).

4.2.5. Synthesis of compound 13

In a two-necked 50 mL round bottomed flask containing 12 mL of absolute ethanol, was added (2-formylphenyl)mercury(II) bromide

(0.20 g, 0.52 mmol). On heating the reaction mixture to 60 °C, a colorless solution was obtained. To it was added dropwise an ethanolic solution (9 mL) of 3-amino-1-propanol (0.04 g, 0.52 mmol) over a period of 10 min. The reaction mixture was refluxed for a period of 52 h to obtain a pale yellowish solution. Then the volume of the reaction mixture was reduced to 5 mL on a rotary evaporator and kept at room temperature to obtain colorless crystals of 13. The lumps of colorless crystals of 13 were collected by filtration, washed with cold benzene, hexane and dried under vacuum (0.16 g, 70% yield). M.p 112-114 °C. Anal. Calcd for C₁₀H₁₂BrHgNO: C, 27.13; H, 2.73; N, 3.16. Found: C, 27.65; H, 2.32; N, 3.70; FT-IR (KBr) 3335, 3062, 2944, 2925, 2874, 2829, 1646, 1434, 1212, 1115, 1072, 756 cm⁻¹; ¹H NMR[#] (400 MHz, CDCl₃) δ 8.50 (s, 1H), 7.52–7.37 (m, 4H), 3.83 (t, J = 6.5 Hz, 2H), 3.78 (t, J = 5.8 Hz, 2H), 2.06–2.00 (m, 2H); ¹³C NMR (400 MHz, CDCl₃) δ 163.7, 163.5, 149.7, 138.9, 137.3, 132.4, 128.8, 60.1, 56.3, 33.2; ES-MS m/z (relative intensity, nature of peak) 443.9 (100, $[M + 1]^+$), 363.9 (30, $[M - Br]^+$; UV–Vis (dichloromethane, λ_{max} nm (cm⁻¹); ε , M⁻¹ cm⁻¹)): 296 (33783); 1479; UV/Vis (solid): λ_{max} : 317 nm; Emission (solid): 420, 442, 456, 483 nm (λ_{ex} 317 nm).

Although, the FT-IR spectrum showed peak for OH group, in ¹H NMR spectrum the peak due to OH proton could not be observed.

4.2.6. Synthesis of compound 14

In a 50 mL, two-necked round bottomed flask, fitted with condenser, hydroxylamine hydrochloride (0.049 g, 0.70 mmol) and NaOH (0.028 g, 0.70 mmol) were taken and dissolved in 5 mL of methanol by stirring at room temperature. This solution was added to a vigorously stirred, methanolic (12 mL) suspension of (2formylphenyl)mercury(II) bromide (0.275 g, 0.71 mmol). The stirring was continued for 4 h at room temperature. The resulting pale yellowish solution was filtered and the solvent was removed completely under reduced pressure. The off-white solid was thoroughly washed with distilled water and dried under vacuum (0.26 g, 91% yield). M.p. 182–185 °C. Anal. Calcd for C₇H₆BrHgNO: C, 20.98; H, 1.50; N, 3.49. Found: C, 21.63; H, 0.98; N, 2.92; FT-IR (KBr) 3397, 1651, 1464, 1440, 1300, 1206, 960, 883, 754 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.21 (s, 1H), 8.16 (br, 1H), 7.47–7.7.43 (m, 1H), 7.39–7.27 (m, 3H); ES-MS m/z (relative intensity, nature of peak) 400.9 (65, [M]⁺, 383.9 (30, [M – OH]⁺); UV–Vis (dichloromethane, λ_{max} nm (cm⁻¹); ε , M⁻¹ cm⁻¹)): 301 (33222); 2063; UV/Vis (solid): λ_{max} : 309 nm; Emission (solid): 421, 445, 483, 520 nm (λ_{ex} 309 nm).

4.2.7. Synthesis of compound 15

To a 50 mL two-necked flask containing 14 mL of absolute ethanol at 70 °C, (2-formylphenyl)mercury(II) bromide (0.22 g, 0.57 mmol) was added. To the colorless solution, an ethanolic solution (5 mL) of ethylenediamine (0.017 g, 0.28 mmol) was added drop-wise for a period of 5 min. After complete addition of the amine solution, the reaction mixture was refluxed 5 h. Then the reaction mixture was filtered hot, washed with hot ethanol and dried under vacuum to obtain **15** as white solid (0.156 g, 69% yield). M.p. 263–264 °C. Anal. Calcd for C₁₆H₁₄Br₂Hg₂N₂: C, 24.16; H, 1.77; N, 3.52. Found: C, 24.50; H, 1.36; N, 4.02; FT-IR (KBr) 2924, 2877, 2848, 1644, 1213, 1031, 1019, 752, 715 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.64 (s, 2H), 7.55–7.38 (m, 8H), 4.21 (s, 4H); ES-MS *m/z* (relative intensity, nature of peak) 347.1 (44, [M + 1H - C₇H₅Br₂Hg]⁺; UV–Vis (dichloromethane, λ_{max} mm (cm⁻¹); ϵ , M⁻¹ cm⁻¹)): 300 (3333); 2300; UV/Vis (solid): λ_{max} : 302 nm; Emission (solid): 396, 465, 489, 527 nm (λ_{ex} 302 nm).

4.2.8. Synthesis of compound 16

To a 50 mL two-necked flask charged with 12 mL of absolute ethanol at 70 $^{\circ}$ C, (2-formylphenyl)mercury(II) bromide (0.20 g, 0.52 mmol) was added and dissolved to obtain a clear solution. To this colorless solution, an ethanolic solution (5 mL) of *trans*-1,2-diaminocyclohexane (0.029 g, 0.26 mmol) was added drop-wise

for a period of 5 min. After complete addition of the amine solution, the reaction mixture was refluxed 7 h at 102 °C. Then the reaction mixture was filtered hot, washed with hot ethanol and dried under vacuum (0.114 g, 52% yield). M.p 246–248 °C. Anal. Calcd for $C_{20}H_{20}Br_2Hg_2N_2$: C, 28.28; H, 2.37, N, 3.30 Found: C, 28.82; H, 1.88; N, 3.92; FT-IR (KBr) 3056, 2996, 2929, 2860, 1641, 1448, 1436, 1211, 762, 716 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.62 (s, 2H), 7.45–7.31 (m, 8H), 4.00 (br, 2H), 1.84–1.61 (m, 8H); ES-MS *m/z* (relative intensity, nature of peak) 850.9 (6, [M + 1]⁺), 491.1 (20, [M - HgBr₂]⁺; UV–Vis (dichloromethane, λ_{max} nm (cm⁻¹); ε , M⁻¹ cm⁻¹)): 300 (33333); 2298; UV/Vis (solid): λ_{max} : 313 nm; Emission (solid): 421, 456, 483, 526 nm (λ_{ex} 313 nm).

4.2.9. Synthesis of compound 17

(2-Formylphenyl)mercury(II) bromide (0.30 g, 0.78 mmol) was taken in a 50 mL two-necked round bottomed flask and 15 mL of absolute ethanol was added to it. It was then heated to 70 $^\circ$ C to obtain a clear solution. To this solution, was added an ethanolic solution (6 mL) of o-phenylenediamine (0.042 g, 0.39 mmol) over a period of 5 min. The resulting reaction mixture was refluxed with stirring for a period 3.5 h. The reaction mixture was filtered hot and the precipitate obtained was washed with hot ethanol and dried under vacuum (0.213 g, 65% yield). M.p 252–254 °C. Anal. Calcd for C₂₀H₁₄Br₂Hg₂N₂: C, 28.48; H, 1.67; N, 3.32; Found: C, 28.79; H, 1.18; N, 2.92. FT-IR (KBr): 3058, 1624, 1576, 1560, 1484, 1293, 1194, 903, 890, 765 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 8.71 (s, 2H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 7.1 Hz, 2H), 7.27–7.54 (m, 8H); ES-MS *m*/*z* (relative intensity, nature of peak) 501.1 (8, $[(M - C_7H_5BrHgN) + K]^+$, 397.1 (15, $[(M - C_{14}H_{10}BrHgN_2) + K]^+$; UV-Vis (dimethylformamide, λ_{max} nm (cm⁻¹); ϵ , M⁻¹ cm⁻¹): 293 (33557); 22557, 351 (28490); 10065; UV/Vis (solid): λ_{max} : 420 nm; Emission (solid): 460, 483, 507, 527 nm (λ_{ex} 420 nm).

4.2.10. Synthesis of compound 18

In a 50 mL two-necked flask, was taken (2-formylphenyl)mercury(II) bromide (0.30 g, 0.78 mmol), 20 mL of absolute ethanol and was heated to 70 °C. To this solution, an ethanolic solution (6 mL) of tris-(2-aminoethyl)amine (0.038 g, 0.26 mmol) was added dropwise at ~100 $^{\circ}$ C for a period of 5 min. The reaction content was refluxed at the same temperature for 24 h. Then the reaction mixture was filtered hot, washed with ethanol and dried under vacuum to obtain 18 as an off-white solid (0.19 g, 58% yield). M.p. 202-204 °C. Anal. Calcd for C₂₇H₂₇Br₃Hg₃N₄: C, 25.96; H, 2.18; N, 4.49. Found: C, 26.29; H, 1.98; N, 5.01; FT-IR (KBr) 3051, 2885, 2846, 1645, 1436, 1211, 758, 716 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.33 (s. 3H), 7.47–6.93 (m, 12H), 3.81 (t, J = 5.2 Hz, 6H), 3.00 (t, J = 5.0 Hz, 6H); ES-MS m/z (relative intensity, nature of peak) 889.0 (3, $[M - HgBr_2]^+$), 800.9 (100, $[M - C_7H_5Br_2Hg]^+$); UV–Vis (dichloromethane, λ_{max} nm (cm⁻¹); ϵ , M⁻¹ cm⁻¹): 307 (32573); 2899; UV/Vis (solid): λ_{max}: 299 nm; Emission (solid): 420, 445, 456, 483, 527 nm (λ_{ex} 299 nm).

4.3. X-ray crystallography

All measurements for **10**, **11**, **12**, **17**, **18** were made on Oxford Diffraction Gemini diffractometer and data collection for **13** was performed on Bruker APEX 2 diffractometer. Data were collected using a graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and full matrix least-squares refinement on F² (program SHELXL-97) [34,35]. Hydrogen atoms were localized by geometrical means. A riding model was chosen for refinement. Crystallographic data and refinement details are given in Tables 3 and 4.

| Ta | hl | P | 3 |
|----|----|---|---|

| X_ray | / CEN | /stall | logr | anhic | narameter | for | 10 | 11 | and | 12 |
|-------|-------|--------|-------|--------|-----------|-----|-----|----|-----|----|
| A-1 d | | stan | וטצונ | aDIIIC | Darameter | 101 | IU. | | anu | 14 |

| | 10 | 11 | 12 |
|---|----------------|---------------------------------------|--|
| Formula | C7H5BrHgO | C ₁₃ H ₁₀ BrHgN | C ₁₀ H ₁₂ BrHgNO |
| Fw | 385.61 | 460.71 | 442.71 |
| Crys. Syst. | Monoclinic | Orthorhombic | Triclinic |
| Space group | P21/c | P212121 | P-1 |
| a, Å | 4.0989(1) | 4.2529(2) | 10.429(3) |
| <i>b</i> , Å | 18.4581(7) | 15.2433(9) | 10.900(3) |
| c, Å | 0.9675(4) | 19.1881(15) | 11.778(2) |
| α | 90 | 90 | 78.80(2) |
| β | 90.824(3) | 90 | 67.34(2) |
| γ | 90 | 90 | 71.34(3) |
| <i>V</i> , Å ³ | 829.69(5) | 1243.93(14) | 1166.7(6) |
| Ζ | 4 | 4 | 4 |
| D/gcm ⁻³ | 3.087 | 2.460 | 2.520 |
| λ | Μο Κα | Μο Κα | Μο Κα |
| | (0.71073 Å) | (0.71073 Å) | (0.71073 Å) |
| T/K | 296 | 295 | 295 |
| μ , mm ⁻¹ | 23.294 | 15.556 | 16.585 |
| Rflc collect/unique | 9761/2739 | 31226/4246 | 26895/7470 |
| R _{int} | 0.057 | 0.119 | 0.076 |
| No.of parms. refined | 92 | 145 | 262 |
| GOF | 1.22 | 1.08 | 1.10 |
| R_1 (obs.), w R_2 | 0.0625, 0.1119 | 0.0718, 0.1758 | 0.0527, 0.1346 |
| $\Delta ho_{\rm max}$, $\Delta ho_{\rm min}/{\rm e}{\rm \AA}^{-3}$ | 2.04, -1.37 | 3.29, -2.17 | 2.11, -1.75 |

5. Computational details

Electronic structure calculations were performed with the Gaussian 03 program [36] by employing the DFT method. All geometries were optimized using Becke three-parameter hybrid exchange functional and Lee–Yang–Parr's gradient corrected correlation functional (B3LYP); 6–31G* basis set was used for H, C, N, O, Br where as SDD basis set with corresponding effective core potential were used for the Hg atom. All stationary points were characterized as minima by evaluating Hessian indices on respective potential energy surfaces. NBO analyses [37,38] on optimized geometry were performed with SDD basis set for Hg and 6-31G(d) for other atoms as implemented in Gaussian 03. NBO picture was generated by using NBOView Software. Time-Dependent Density

X-ray crystallographic parameter for 13, 17 and 18

| | 13 | 17 | 18 |
|---|--|--|--|
| Formula | C ₂₂ H ₂₈ Br ₂ Hg ₂ N ₄ | C ₂₀ H ₁₄ Br ₂ Hg ₂ N ₂ | C ₂₇ H ₂₇ Br ₃ Hg ₃ N ₄ , |
| | | | CH ₂ Cl ₂ |
| Fw | 909.48 | 843.33 | 1333.92 |
| Crys. Syst. | Triclinic | Monoclinic | Monoclinic |
| Space group | P-1 | C2/c | P21/c |
| a, Å | 8.5443(15) | 15.256(19) | 11.3588(3) |
| <i>b</i> , Å | 8.8775(16) | 9.648(2) | 20.3061(4) |
| <i>c</i> , Å | 9.7046(17) | 14.640(1) | 15.6492(3) |
| α | 113.982(2) | 90 | 90 |
| β | 90.112(2) | 111.222(4) | 104.092(2) |
| γ | 108.450(2) | 90 | 90 |
| V, Å ³ | 630.71(19) | 2009(3) | 3500.91(14) |
| Ζ | 1 | 4 | 4 |
| D/gcm ⁻³ | 2.395 | 2.788 | 2.531 |
| λ | Μο Κα | Μο Κα | Μο Κα |
| | (0.71073 Å) | (0.71073 Å) | (0.71073 Å) |
| T/K | 293 | 295 | 295 |
| μ , mm ⁻¹ | 15.340 | 19.252 | 16.724 |
| Rflc collect/ | 7193/3550 | 8467/3168 | 55326/11630 |
| unique | | | |
| R _{int} | 0.043 | 0.078 | 0.118 |
| No.of parms. refined | 138 | 118 | 357 |
| GOF | 1.06 | 0.90 | 1.09 |
| $R_1(obs.), wR_2$ | 0.0406. 0.1061 | 0.0584. 0.1289 | 0.0796. 0.1470 |
| $\Delta \rho_{\rm max}$, $\Delta \rho_{\rm min}/{\rm e}{\rm \AA}^{-3}$ | 3.72, -4.89 | 2.66, -1.27 | 2.17, -1.89 |

Functional theory was employed on optimized geometry for evaluating singlet excited states and corresponding oscillator strengths. Atoms in molecules (AIM) analysis [39] was carried out by AIM2000 [40] on the wavefunction file generated from Gaussian 03. WTBS basis set was employed for Hg and 6–31G* basis set was employed for remaining atoms in AIM analysis.

Acknowledgments

We are grateful to the Department of Science and Technology (DST), New Delhi for the Ramanna Fellowship. S.S. is thankful to UGC New Delhi for SRF.

Appendix A. Supplementary material

CCDC 777015, 777017, 777016, 777018, 777019 and 777020 contain the supplementary crystallographic data for **10**, **11**, **12**, **13**, **17** and **18**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary material

Supplementary data associated with this article can be found, in online version, at doi:10.1016/j.jorganchem.2011.06.001.

References

- [1] E.C. Constable, T.A. Leese, J. Organomet. Chem. 335 (1987) 293–299.
- [2] S. Attar, J.H. Nelson, J. Fischer, A. de Cian, J.P. Sutter, M. Pfeffer, Organometallics 14 (1995) 4559–4569.
- [3] S. Attar, V.J. Catalano, J.H. Nelson, Organometallics 15 (1996) 2932–2946.
 [4] Y. Wu, L. Ding, Z.X. Zhou, C.X. Du, W.L. Wang, J. Organomet. Chem. 564 (1998) 233–239.
- [5] A. Berger, A. de. Cian, J.P. Djukic, J. Fischer, M. Pfeffer, Organometallics 20 (2001) 3230–3240.
- [6] A. Berger, J.P. Djukic, M. Pfeffer, J. Lacour, L. Vial, A.D. Cian, N.K. Gruber, Organometallics 22 (2003) 5243–5260.
- [7] H.X. Wang, Y.J. Li, H.F. Wu, R.Q. Gao, F.Y. Geng, X.L. Yang, L. Wan, R. Jin, X.L. Cui, Y.J. Wu, Polyhedron 25 (2006) 3305–3311.
- [8] S.D.J. Brown, W. Henderson, K.J. Kilpin, B.K. Nicholson, Inorg. Chim. Acta. 360 (2007) 1310–1315.
- [9] K.J. Kiĺpin, R.A. Linklater, W. Henderson, B.K. Nicholson, Inorg. Chim. Acta. 363 (2010) 1021–1030 (and references therein).
- [10] S. Attar, J.H. Nelson, J. Fischer, Organometallics 14 (1995) 4776-4780.
- [11] N. Gül, J.H. Nelson, J. Mol. Struct. 475 (1999) 121–130.
- [12] Y. Liu, P.-F. Yan, Y.-H. Yu, G.-F. Hou, J.-S. Gao, Inorg. Chem. Commun. 13 (2010) 630–632 (and references therein).
- [13] E.C. Constable, T.A. Leese, D.A. Tocher, J. Chem. Soc. Chem.Commun. (1989) 570–571.

- [14] M. Ali, W.R. McWhinnie, T.A. Hamor, J. Organomet. Chem. 371 (1989) C37-C39.
- [15] O. Bumbu, C. Silvestru, M.C. Gimeno, A. Lugana, J. Organomet. Chem. 689 (2004) 1172–1179.
- [16] D.W. Slocum, T.R. Engelmann, J. Organomet. Chem. 24 (1970) 753.
- [17] L.G. Kuz'mina, Yu.T. Štruchkov, L.L. Troitskaya, V.I. Sokolov, J. Strukt. Chem. (USSR) 26 (1985) 428.
 [18] N. Seidel, K. Jacob, A.K. Fischer, K. Merzweiler, C. Wagner, M. Fontani,
- P. Zanello, J. Organomet. Chem. 630 (2001) 149–156.
- [19] S.Q. Huo, Y.J. Wu, Y. Zhu, L. Yang, J. Organomet. Chem. 470 (1994) 17–22.
 [20] U. Patel, H.B. Singh, G. Wolmershäuser, Angew. Chem. Int. Ed 44 (2005)
- 1715–1717.
- [21] S. Sharma, R.S. Baligar, H.B. Singh, R.J. Butcher, Angew. Chem. Int. Ed. 48 (2009) 1987–1990.
- [22] S.D. Apte, S.S. Zade, H.B. Singh, R.J. Butcher, Organometallics 22 (2003) 5473-5477.
- [23] K.R. Flower, V.J. Howard, S. Naguthney, R.G. Pritchard, J.E. Warren, A.T. McGown, Inorg. Chem. 41 (2002) 1907–1912.
 [24] R.J. Evans, K.R. Flower, L.G. Leal, P.J. O'Malley, C. Mangold, R.G. Pritchard,
- J.E. Warren, J. Organomet. Chem. 692 (2007) 2519–2528.
- [25] C.E.F. Rickard, W.R. Roper, F. Tutone, S.D. Woodgate, L.J. Wright, J. Organomet. Chem. 619 (2001) 293–298.
- [26] A.J. Canty, G.B. Deacon, Inorg. Chim. Acta. 45 (1980) L225-L227.
- [27] S.S. Batsanov, Inorg. Mater. 36 (2001) 1031-1046.
- [28] A. Bondi, J. Phys. Chem. 68 (1964) 441-451.
- [29] B. Cordero, V. Gómez, A.E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, S. Alvarez, Dalton Trans. (2008) 2832–2838.
- [30] D.St.C. Black, G.B. Deacon, G.L. Edwards, B.M. Gatehouse, Aust. J. Chem. 46 (1993) 1323–1336.
- [31] J.L. Atwood, D.E. Berry, S.R. Stobart, M.L. Zaworotko, Inorg. Chem. 22 (1983) 3480–3482.
- [32] J.-Y. Wu, H.-Y. Hsu, C.-C. Chan, Y.-S. Wen, C. Tsai, K.-L. Lu, Inorg. Chem. 9 (2009) 258–262.
- [33] M.S. Bharara, T.H. Bui, S. Parkin, D.A. Atwood, Dalton. Trans. (2005) 3874–3880 (and references therein).
- [34] G.M. Sheldrick, SHELXS-97, Program for Crystal Structures Solution. University of Göttingen, Göttingen, Germany, 1997.
- [35] G.M. Sheldrick, SHELXL-97, Program for Crystal Structures Refinement. University of Göttingen, Göttingen, Germany, 1997.
- [36] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, AJ. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN03, Revision C.02. Gaussian, Inc., Wallingford, CT, 2004.
- [37] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899-926.
- 38] E.D. Glendening, A.E. Reed, J.E. Carpenter, F. Weinhold, NBO Version 3.1.
- [39] R.F.W. Bader, Atoms in Molecules: A Quantum Theory. Oxford University Press, New York, 1990.
- [40] F. Biegler-König, J. Schönbohm, D. Bayles, J. Comput. Chem. 22 (2001) 545–559.